

What is claimed is:

- 1 A catalyst composition suitable for use as a catalyst for the preparation of an ester comprising
 - (a) an organometallic compound which is the reaction product of an orthoester or condensed orthoester of at least one metal selected from titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups, and an organophosphorus compound containing at least one P-OH group, and
 - (b) at least one compound of germanium, antimony or tin.
- 2 A catalyst composition according to claim 1 characterized in that the organometallic compound comprises the reaction product of an orthoester or condensed orthoester of at least one metal selected from titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups, an organophosphorus compound containing at least one P-OH group, and a base.
- 3 A catalyst composition according to claim 1 or claim 2 characterized in that the organometallic compound comprises the reaction product of an orthoester or condensed orthoester of at least one metal selected from titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups, an organophosphorus compound containing at least one P-OH group, a base and a 2-hydroxy carboxylic acid.
- 4 A catalyst composition according to claim 3 characterized in that the 2-hydroxy acid is lactic acid, citric acid, malic acid or tartaric acid or a phosphorus derivative of at least one of said acids.
- 5 A catalyst composition according to claim 1, characterized in that the orthoester has the formula $M(OR)_4$ and/or $Al(OR)_3$ where M is titanium and/or zirconium and R is an alkyl group containing from 1 to 6 carbon atoms.
- 6 A catalyst composition according to claim 1 characterized in that the condensed orthoester has a structure which can be represented by the formula, $R^1O[M(OR^1)_2O]_nR^1$ where M is titanium and/or zirconium, R^1 is an alkyl group containing 1 to 6 carbon atoms and n is less than 20.
- 7 A catalyst composition according to claim 1, characterized in that the alcohol containing at least two hydroxyl groups is 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2-methyl-2,4-pentanediol, diethylene glycol, polyethylene glycol, glycerol, trimethylolpropane, pentaerythritol or 1,6 cyclohexane dimethanol.

8. A catalyst composition according to claim 1, characterized in that the organometallic compound is prepared by reacting a dihydric alcohol with an orthoester or condensed orthoester in a ratio of from 1 to 32 moles of dihydric alcohol to each mole of titanium, zirconium or aluminium.
9. A catalyst composition according to claim 1, characterized in that the organophosphorus compound is a phosphate, a pyrophosphate, a phosphonate, a phosphinate, a phosphite or a salt of a phosphate or phosphonate or a phosphorous derivative of a hydroxy acid..
10. A catalyst composition according to claim 9, characterized in that the organophosphorus compound is a substituted or unsubstituted alkyl phosphate, a substituted or unsubstituted aryl phosphate, a salt of an alkyl or aryl phosphonate, a phosphate of an alkylaryl glycol ether or an alkyl glycol ether, or a product obtainable by reaction of phosphorus pentoxide with a polyhydric alcohol.
11. A catalyst composition according to claim 10, characterized in that the organophosphorus compound is an alkyl phosphate in which the organic group contains up to 20 carbon atoms.
12. A catalyst composition according to claim 10, characterized in that the organophosphorus compound is a phosphate of an alkylaryl glycol ether or an alkyl glycol ether having a carbon chain length up to 18 carbon atoms.
13. A catalyst composition according to claim 10, characterized in that the organophosphorus compound is a reaction product of phosphorus pentoxide and a polyhydric alcohol in which the molar ratio of polyhydric alcohol to P is up to 50:1.
14. A catalyst composition according to claim 9, characterized in that the organophosphorus compound is a phosphorous derivative of a hydroxy acid
15. A catalyst composition according to claim 1, characterized in that the organophosphorus compound is present in the organometallic compound in an amount in the range 0.1 to 4.0 mole of phosphorus to 1 mole of titanium, zirconium or aluminium.

16. A catalyst composition according to claim 1, characterized in that a base is present in the organometallic compound in an amount in the range 0.01 to 4.0 mole of base to 1 mole of titanium, zirconium or aluminium.
17. A catalyst composition according to claim 3, characterized in that the 2-hydroxy acid is present in the organometallic compound in an amount in the range 0.1 to 4 mole acid to 1 mole of titanium, zirconium or aluminium.
18. A catalyst composition according to claim 1, characterized in that the compound of germanium is germanium dioxide or a salt of germanium.
19. A catalyst composition according to claim 1, characterized in that the compound of antimony is antimony trioxide or a salt of antimony.
20. A catalyst composition according to claim 1, characterized in that the compound of tin is a tin salt, a dialkyl tin oxide, a dialkyl tin dialkanoate or an alkylstannoic acid.
21. A catalyst composition according to claim 1, characterized in that the molar ratio of the organometallic compound to the compound of germanium, antimony or tin is in the range 9 : 1 to 1 : 9 calculated as moles of Ti, Zr or Al to moles of Ge, Sb or Sn.
22. A process for the preparation of an ester comprising carrying out an esterification reaction in the presence of a catalyst composition comprising
 - (a) the reaction product of an orthoester or condensed orthoester of at least one metal selected from titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups, an organophosphorus compound containing at least one P-OH group and optionally a base, and
 - (b) at least one compound of germanium, antimony or tin.
23. A process according to claim 22 characterized in that the esterification reaction comprises reaction of an alcohol with stearic acid, isostearic acid, capric acid, caproic acid, palmitic acid, oleic acid, palmitoleic acid, triacontanoic acid, benzoic acid, methyl benzoic acid, salicylic acid, a rosin acid, abietic acid, phthalic acid, isophthalic acid, terephthalic acid, sebacic acid, adipic acid, azelaic acid, succinic acid, fumaric acid, maleic acid, naphthalene dicarboxylic acid, pamoic acid, trimellitic acid, citric acid, trimesic acid or pyromellitic acid.

24. A process according to claim 22 characterized in that the esterification reaction comprises a reaction of an alcohol with an anhydride of a dicarboxylic acid or a tricarboxylic acid.
25. A process according to claim 22 characterized in that the esterification reaction comprises reaction of a methyl ester, an ethyl ester or a propyl ester of acrylic acid or methacrylic acid with an alcohol.
26. A process according to claim 22 characterized in that the esterification reaction comprises reaction of two esters to produce two different esters by exchange of alkoxy groups.
27. A process according to claim 22 characterized in that the esterification reaction comprises a polyesterification comprising the reaction of terephthalic acid, dimethyl terephthalate, dimethyl naphthalenate or naphthalene dicarboxylic acid with 1,2-ethanediol, 1,4-butanediol, 1,3-propanediol, 1,6 cyclohexane dimethanol, trimethylolpropane or pentaerythritol.
28. A process according to claim 22 characterized in that the catalyst is present in an amount in the range 10 to 1200 parts per million calculated as parts by weight of total metal (Ti, Zr or Al plus Ge, Sb or Sn) with respect to weight of product ester.
29. A process according to claim 22 or 27 characterized in that the esterification reaction is a polyesterification and the catalyst is present in an amount in the range 5 to 550 parts per million calculated as parts by weight total metal (Ti, Zr or Al plus Ge, Sb or Sn) with respect to weight of product polyester.
30. A process according to claim 22, characterized in that the catalyst composition is present in an amount such that the total amount of titanium, zirconium or aluminium present is in the range 5 to 500 parts per million calculated as parts by weight of Ti, Zr or Al with respect to weight of product ester and the total amount of germanium, antimony or tin present is in the range 5 to 700 ppm calculated as Ge, Sb or Sn with respect to product ester.
31. A process according to claim 22, characterized in that the catalyst composition is present in an amount such that the total amount of titanium, zirconium or aluminium present is in the range 3 to 250 parts per million calculated as parts by weight of Ti, Zr or Al with respect to weight of product polyester and the total amount of germanium,

antimony or tin present is in the range 3 to 300 ppm calculated as Ge, Sb or Sn with respect to product polyester.

32. A polyester comprising the residues of a reaction between a polybasic acid or ester thereof with a polyhydric alcohol and further containing residues of a catalyst system comprising:

- (a) the reaction product of an orthoester or condensed orthoester of at least one metal selected from titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups and an organophosphorus compound containing at least one P-OH group, and
- (b) at least one compound of germanium, antimony or tin.

CLAIMS

1. A catalyst composition suitable for use as a catalyst for the preparation of an ester comprising
 - (a) an organometallic compound which is the reaction product of an orthoester or condensed orthoester of at least one metal selected from titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups, and an organophosphorus compound containing at least one P-OH group, and
 - (b) at least one compound of germanium, antimony or tin.
2. A catalyst composition according to claim 1 characterised in that the organometallic compound comprises the reaction product of an orthoester or condensed orthoester of at least one metal selected from titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups, an organophosphorus compound containing at least one P-OH group, and a base.
3. A catalyst composition according to claim 1 or claim 2 characterised in that the organometallic compound comprises the reaction product of an orthoester or condensed orthoester of at least one metal selected from titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups, an organophosphorus compound containing at least one P-OH group, a base and a 2-hydroxy carboxylic acid.
4. A catalyst composition according to claim 3 characterised in that the 2-hydroxy acid is lactic acid, citric acid, malic acid or tartaric acid or a phosphorus derivative of at least one of said acids.

5. A catalyst composition according to any one of the preceding claims characterised in that the orthoester has the formula $M(OR)_4$ and/or $Al(OR)_3$ where M is titanium and/or zirconium and R is an alkyl group containing from 1 to 6 carbon atoms.
6. A catalyst composition according to any one of claims 1, 2 and 3 characterised in that the condensed orthoester has a structure which can be represented by the formula, $R^1O[M(OR^1)_{20}]R_n$ where M is titanium and/or zirconium, R^1 is an alkyl group containing 1 to 6 carbon atoms and n is less than 20.
7. A catalyst composition according to any one of the preceding claims characterised in that the alcohol containing at least two hydroxyl groups is 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2-methyl- 2,4-pentanediol, diethylene glycol, polyethylene glycol, glycerol, trimethylolpropane, pentaerythritol or 1,6 cyclohexane dimethanol.
8. A catalyst composition according to any one of the preceding claims characterised in that the organometallic compound is prepared by reacting a dihydric alcohol with an orthoester or condensed orthoester in a ratio of from 1 to 32 moles of dihydric alcohol to each mole of titanium, zirconium or aluminium.
9. A catalyst composition according to any one of the preceding claims characterised in that the organophosphorus compound is a phosphate, a pyrophosphate, a phosphonate, a phosphinate, a phosphite or a salt of a phosphate or phosphonate or a phosphorous derivative of a hydroxy acid..
10. A catalyst composition according to any one of the preceding claims characterised in that the organophosphorus compound is a substituted or unsubstituted alkyl phosphate, a substituted or unsubstituted aryl phosphate, a salt of an alkyl or aryl phosphonate, a phosphate of an

alkylaryl glycol ether or an alkyl glycol ether, or a product obtainable by reaction of phosphorus pentoxide with a polyhydric alcohol.

11. A catalyst composition according to any one of the preceding claims characterised in that the organophosphorus compound is an alkyl phosphate in which the organic group contains up to 20 carbon atoms.
12. A catalyst composition according to any one of claims 1 to 10 characterised in that the organophosphorus compound is a phosphate of an alkylaryl glycol ether or an alkyl glycol ether having a carbon chain length up to 18 carbon atoms.
13. A catalyst composition according to any one of claims 1 to 10 characterised in that the organophosphorus compound is a reaction product of phosphorus pentoxide and a polyhydric alcohol in which the molar ratio of polyhydric alcohol to P is up to 50:1.
14. A catalyst composition according to any one of claims 1 to 10 characterised in that the organophosphorus compound is a phosphorous derivative of a hydroxy acid.
15. A catalyst composition according to any one of the preceding claims characterised in that the organophosphorus compound is present in the organometallic compound in an amount in the range 0.1 to 4.0 mole of phosphorus to 1 mole of titanium, zirconium or aluminium.
16. A catalyst composition according to any one of the preceding claims characterised in that a base is present in the organometallic compound in an amount in the range 0.01 to 4.0 mole of base to 1 mole of titanium, zirconium or aluminium.

17. A catalyst composition according to any one of claims 3 to 16 characterised in that the 2-hydroxy acid is present in the organometallic compound in an amount in the range 0.1 to 4 mole acid to 1 mole of titanium, zirconium or aluminium.
18. A catalyst composition according to any one of the preceding claims characterised in that the compound of germanium is germanium dioxide or a salt of germanium.
19. A catalyst composition according to any one of the preceding claims characterised in that the compound of antimony is antimony trioxide or a salt of antimony.
20. A catalyst composition according to any one of the preceding claims characterised in that the compound of tin is a tin salt, a dialkyl tin oxide, a dialkyl tin dialkanoate or an alkylstannoic acid.
21. A catalyst composition according to any one of the preceding claims characterised in that the molar ratio of the organometallic compound to the compound of germanium, antimony or tin is in the range 9 : 1 to 1 : 9 calculated as moles of Ti, Zr or Al to moles of Ge, Sb or Sn.
22. A process for the preparation of an ester comprising carrying out an esterification reaction in the presence of a catalyst composition comprising
 - (a) the reaction product of an orthoester or condensed orthoester of at least one metal selected from titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups, an organophosphorus compound containing at least one P-OH group and optionally a base, and
 - (b) at least one compound of germanium, antimony or tin.
23. A process according to claim 22 characterised in that the esterification reaction comprises reaction of an alcohol with stearic acid, isostearic acid, capric acid, caproic acid, palmitic acid,

oleic acid, palmitoleic acid, triacontanoic acid, benzoic acid, methyl benzoic acid, salicylic acid, a rosin acid, abietic acid, phthalic acid, isophthalic acid, terephthalic acid, sebacic acid, adipic acid, azelaic acid, succinic acid, fumaric acid, maleic acid, naphthalene dicarboxylic acid, pamoic acid, trimellitic acid, citric acid, trimesic acid or pyromellitic acid.

24. A process according to claim 22 characterised in that the esterification reaction comprises a reaction of an alcohol with an anhydride of a dicarboxylic acid or a tricarboxylic acid.
25. A process according to claim 22 characterised in that the esterification reaction comprises reaction of a methyl ester, an ethyl ester or a propyl ester of acrylic acid or methacrylic acid with an alcohol.
26. A process according to claim 22 characterised in that the esterification reaction comprises reaction of two esters to produce two different esters by exchange of alkoxy groups.
27. A process according to claim 22 characterised in that the esterification reaction comprises a polyesterification comprising the reaction of terephthalic acid, dimethyl terephthalate, dimethyl naphthalenate or naphthalene dicarboxylic acid with 1,2-ethanediol, 1,4-butanediol, 1,3-propanediol, 1,6 cyclohexane dimethanol, trimethylolpropane or pentaerythritol.
28. A process according to any one of claims 22 to 26 characterised in that the catalyst is present in an amount in the range 10 to 1200 parts per million calculated as parts by weight of total metal (Ti, Zr or Al plus Ge, Sb or Sn) with respect to weight of product ester.
29. A process according to claim 22 or 27 characterised in that the esterification reaction is a polyesterification and the catalyst is present in an amount in the range 5 to 550 parts per million calculated as parts by weight total metal (Ti, Zr or Al plus Ge, Sb or Sn) with respect to weight of product polyester.

30. A process according to any one of claims 22 to 26 and 28 characterised in that the catalyst composition is present in an amount such that the total amount of titanium, zirconium or aluminium present is in the range 5 to 500 parts per million calculated as parts by weight of Ti, Zr or Al with respect to weight of product ester and the total amount of germanium, antimony or tin present is in the range 5 to 700 ppm calculated as Ge, Sb or Sn with respect to product ester.

31. A process according to any one of claims 22, 27 or 29 characterised in that the catalyst composition is present in an amount such that the total amount of titanium, zirconium or aluminium present is in the range 3 to 250 parts per million calculated as parts by weight of Ti, Zr or Al with respect to weight of product polyester and the total amount of germanium, antimony or tin present is in the range 3 to 300 ppm calculated as Ge, Sb or Sn with respect to product polyester.

32. A polyester comprising the residues of a reaction between a polybasic acid or ester thereof with a polyhydric alcohol and further containing residues of a catalyst system comprising:

- (a) the reaction product of an orthoester or condensed orthoester of at least one metal selected from titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups and an organophosphorus compound containing at least one P-OH group, and
- (b) at least one compound of germanium, antimony or tin.